



Engineering, Operations & Technology  
Boeing Research & Technology

# Non-Cr paint systems on commercial aircraft – current status and future direction

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# Overview

## Boeing Commercial Airplanes

### **Cr<sup>6+</sup> Overview**

**Historic & Current use of Cr<sup>6+</sup>**

**Chromate use and alternatives**

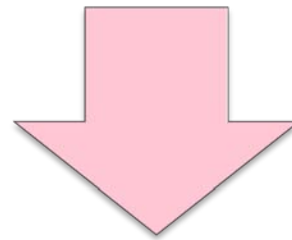
**Strategy for Sunset Date**

**Near term systems and qualifications**

**Gaps and long term developments**

# Cr<sup>6+</sup> Overview

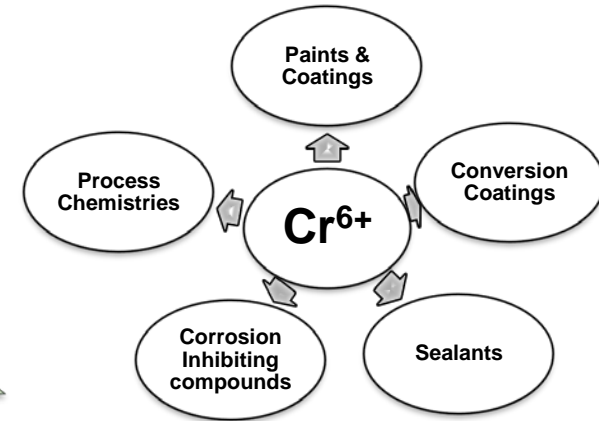
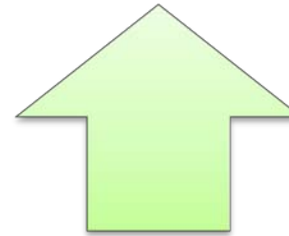
Cr<sup>6+</sup> is a known carcinogen and an excellent corrosion inhibitor



**Gold  
Standard of  
Corrosion  
Inhibitors**

**Carcinogenic**

- REACH Sunset Date 2017-2019
- Hazardous Waste
- OSHA Permissible Exposure Limit 5 µg/m<sup>3</sup>



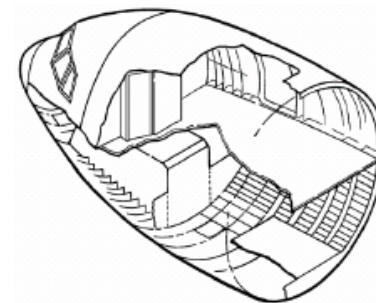
# Historic & Current use of Cr<sup>6+</sup> Boeing Commercial Airplanes

**Cr<sup>6+</sup> containing materials have been used on all metal parts, including aluminum, titanium, and stainless steel alloys.**

**Over 75% of the plane is coated with chromated materials.**

## Successful Cr<sup>6+</sup> reductions via:

- Substrates and Design changes (composite materials, titanium, guidelines, etc.)
- Alternative materials (products and processes)



Item	Division	Sub-division	Surface of part	Location on airplane	Finish requirement
Bare plate and sheet, extruded shapes, extruded bar drawn or rolled bar, forged block, forgings and castings <b>FN 3</b>				Fuselage lower lobe <b>FN 1</b>	Anodize + two coats BMS 10-11 Type I primer
				Fuselage upper lobe	Anodize + BMS 10-11 Type I primer
				Nonaero-dynamic exterior	Anodize + BMS 10-11 Type I primer
				Exterior Aerodynamic	Anodize + BMS 10-79 Type III primer + BMS 10-60 Type II white enamel or BMS10-126 Type II
				Landing gear	Anodize + BMS 10-79 Type III primer + BMS 10-60 Type II gray enamel
Attached to CFRP <b>FN 8</b> <b>FN 3</b>			Within 4 in of CFRP <b>FN 54</b>	General except as noted below	Anodize + two coats BMS 10-11 Type I primer
				Located in integral fuel tank	Anodize + two coats BMS 10-20 Type II primer
				Exterior Aerodynamic, Wing and empennage trailing edge coves	Anodize + two coats BMS 10-79 Type III primer

**Corrosion Potential Table**

Group	Metal or alloy
I	Magnesium and its alloys
II	Aluminum, zinc, and their alloys. Cadmium-titanium, cadmium or zinc-nickel plating
III	Steels (except CRES), Iron, lead, tin, and their alloys. Tin plating.
IV	CFRP, titanium and titanium alloys, CRES, bronze (aluminum-bronze or aluminum-nickel-bronze), nickel and nickel alloys, chromium (plating), copper, brass, copper-nickel, copper-beryllium, molybdenum, cobalt alloys, tungsten, carbon, silver, and gold

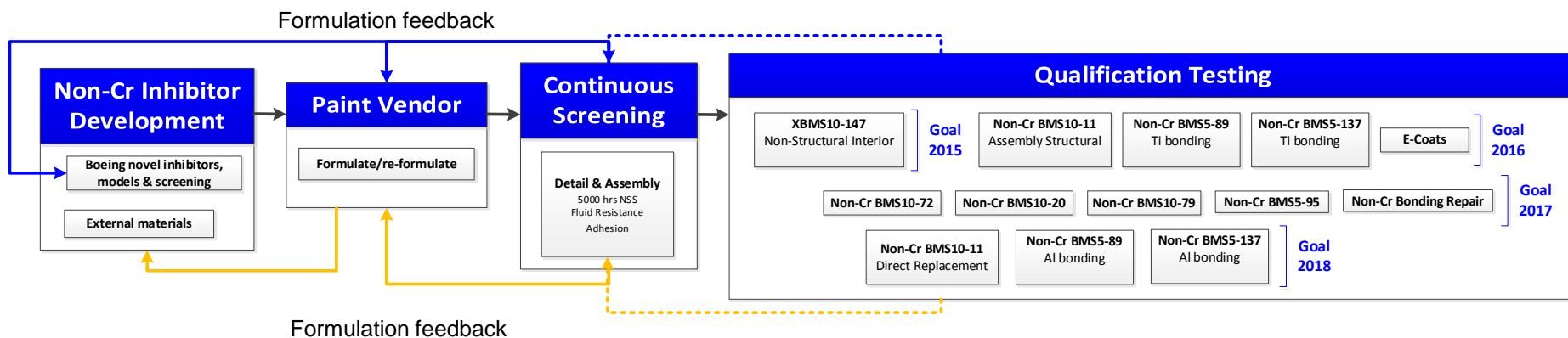
# Chromate Alternative Successes and Targets

Chromated material/process	Alternatives
Chromic acid anodize	Boric sulfuric acid anodize (BSAA), Accelerated sulfuric acid anodize (ASAA)
Deoxidizers	Ferric/nitric deoxidizers
Paint strippers	Mechanical, benzyl alcohol based. In work: laser & atmospheric plasma
Composite primers	BMS10-103
Exterior primer (BMS10-72, MIL-PRF-23377)	BMS10-72 NC In work: searching for Cr <sup>6+</sup> equivalency
Non-structural interior primer (BMS10-11 Ty I lite)	In work: XBMS10-147
Structural interior primer (BMS10-11 Ty I, MIL-PRF-85582, MIL-PRF-23377)	In work
Bond primer (BMS5-89, BMS5-137)	In work
Assembly level primer	In work
BMS10-20 (SAE-AMS-C-27725)	In work
BMS10-79	In work
BMS5-95	In work

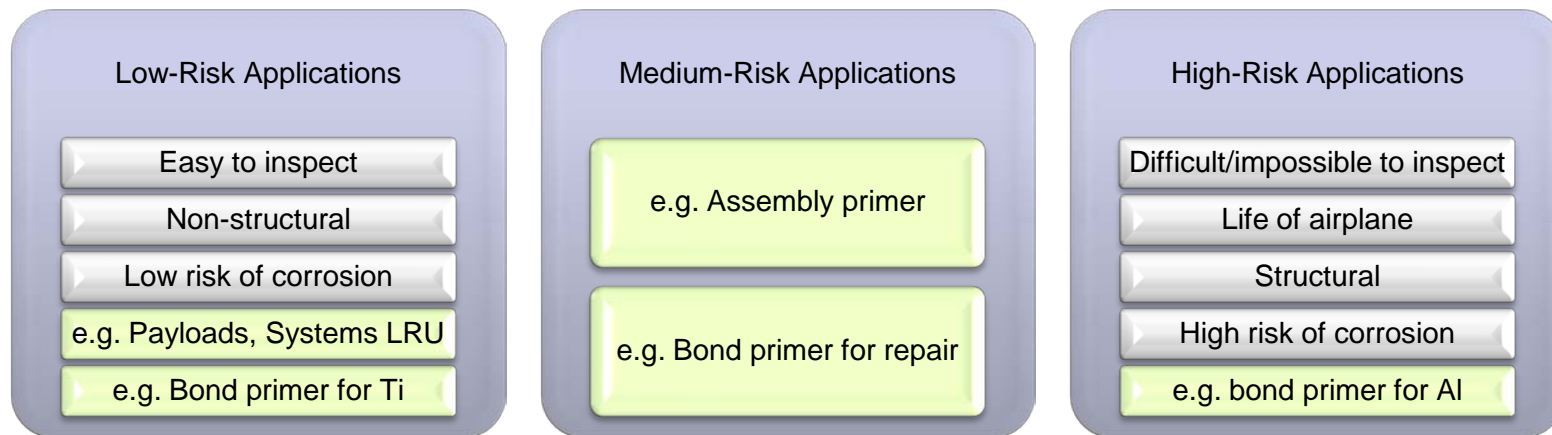
# Strategy for Sunset Date

Non-Cr for BMS10-11, BMS10-20, BMS10-72/BMS10-79, BMS5-89

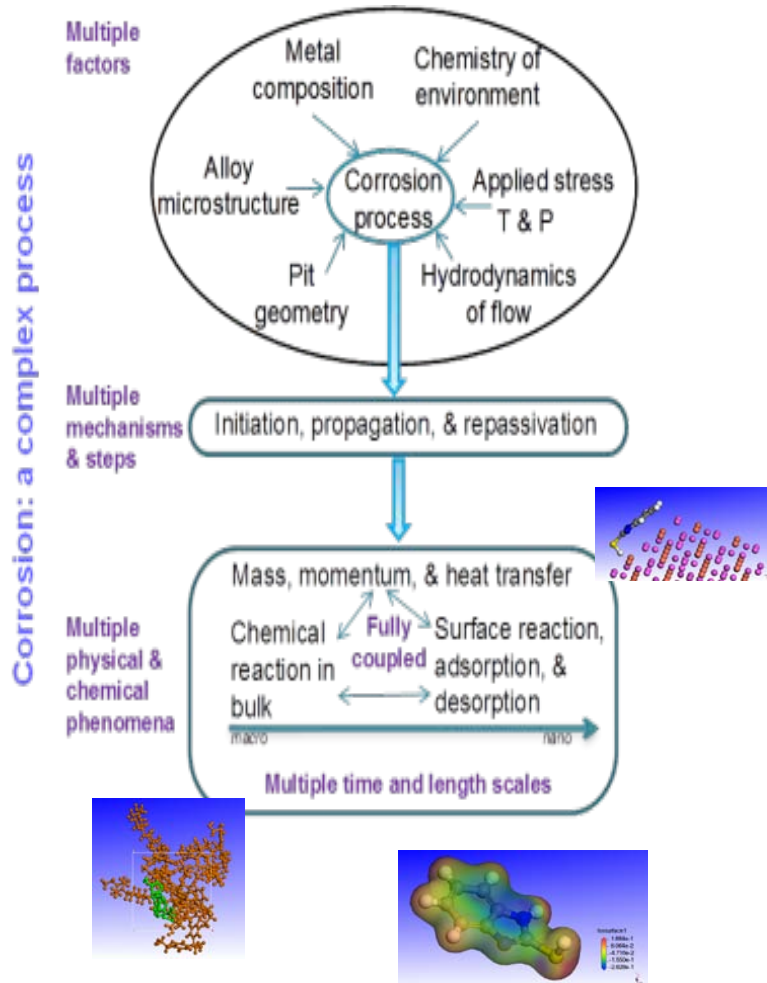
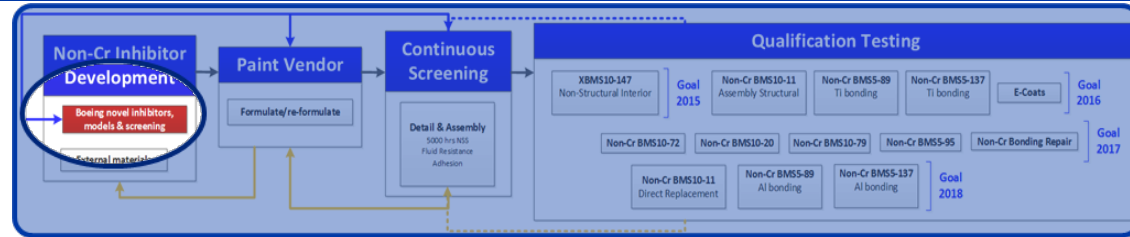
## Multidimensional approach:



**Test top candidates to the spec requirements, match product performance to application.**



# Corrosion Protection System Development



## Materials development

- CSIRO, Boeing, Suppliers, universities
- Inhibitor species
- Polymer resins
- Formulation nuances

## Testing/evaluation

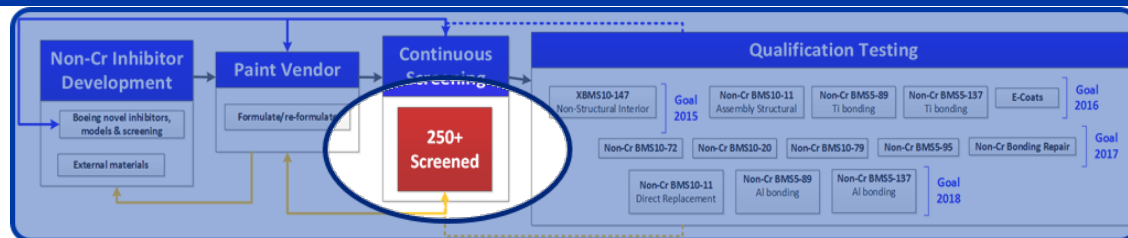
- Boeing, universities, CSIRO
- Accelerated exposure protocols
- Advanced evaluation techniques

## Modeling tools

- Boeing, CSIRO, universities
- Inhibitor mechanisms
- Transport processes
- Service performance prediction



# Continuous Screening Overview



## Materials Process Example:



## Test panel stack-ups:

### Detail Primer:

7075-T6 Bare Al
Alodine 600 BSAA Unsealed BMS10-128
BMS10-11 Ty I Green or Candidate

### Assembly Primer:

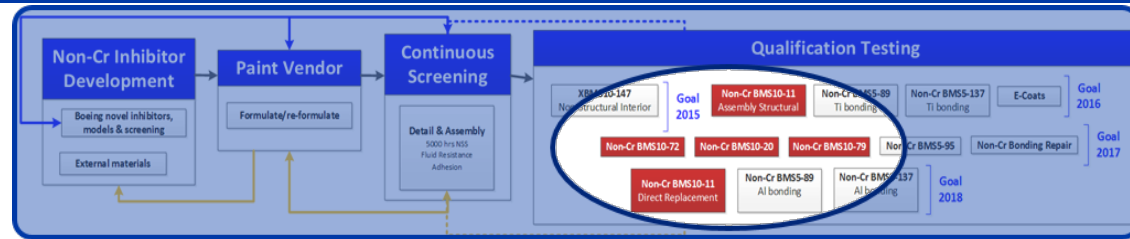
7075-T6 Bare Al
Alodine 600 BSAA Unsealed BMS10-128
BMS10-11 Ty I Green
BMS10-11 I Yellow or Candidate

## Screening Tests:

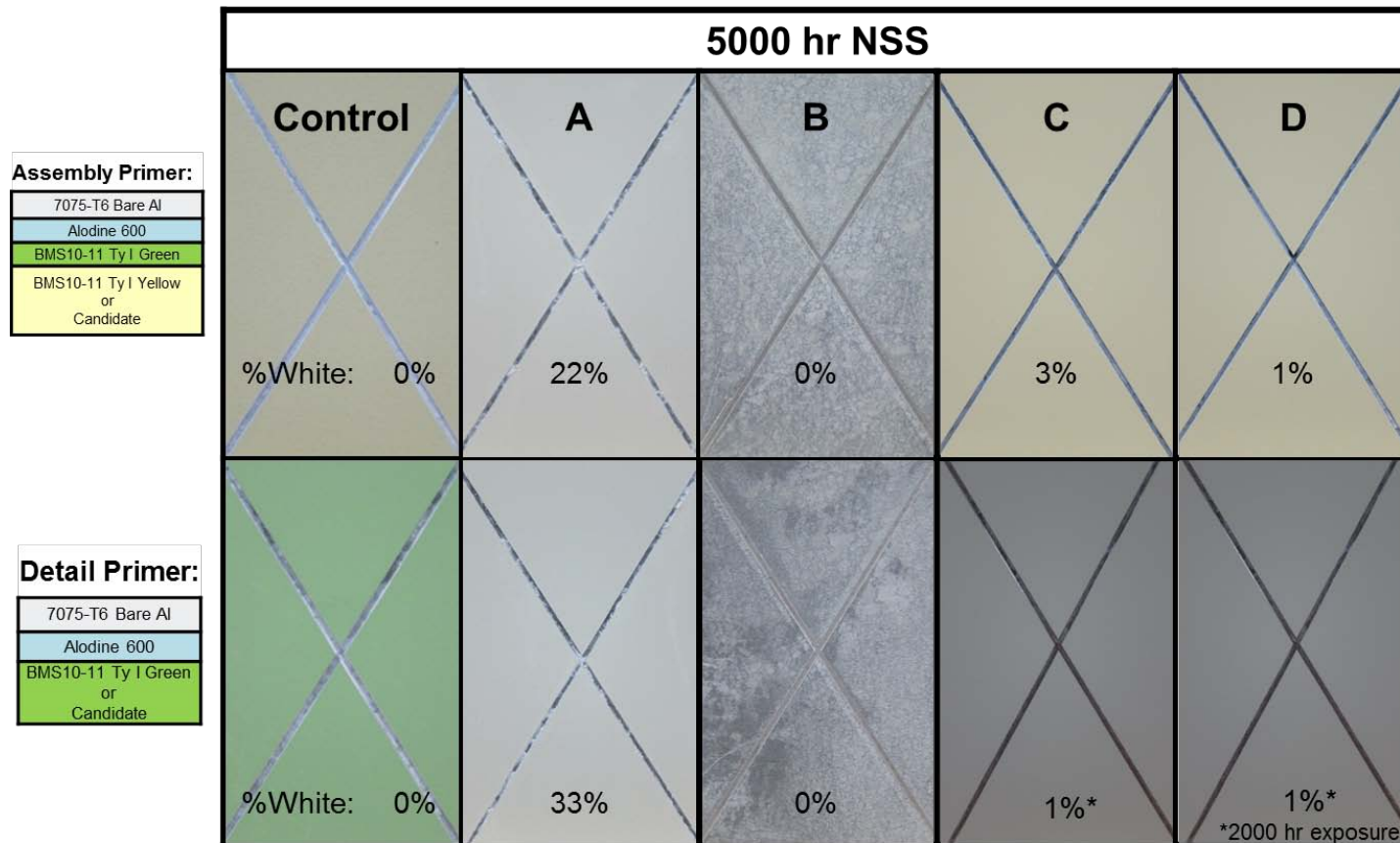
- Dry/Wet Adhesion. BSS7225, ASTM D 714.
- 30 days 120F condensing humidity. BSS7225, ASTM D 714
- 30 day hydraulic fluid soak. BSS7263, ASTM D 714
- 5000 hours in Neutral Salt Spray chamber. BSS7249, ASTM D 714

**Candidates that look good in screening, move to production batch testing**

# Continuous Screening Medium/High risk zones



Four candidates are moving to production batch testing to  
BMS10-11 Ty I, BMS10-20, BMS10-72, & BMS10-79



# XBMS10-147

## Low-corrosion risk zones

### Technical Requirements

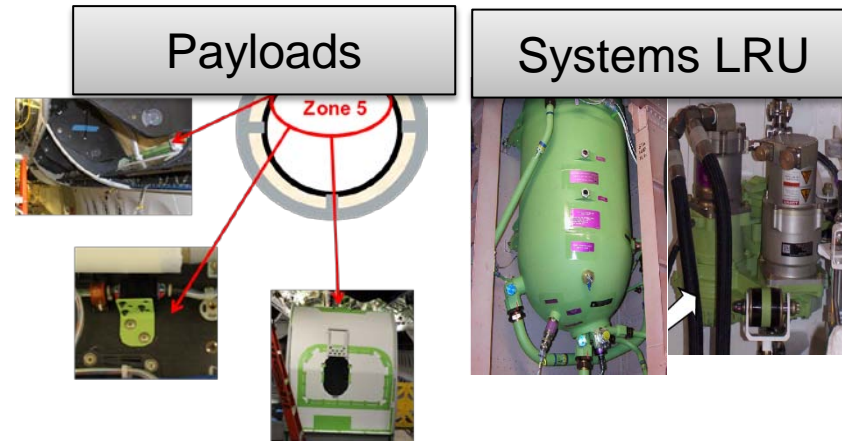
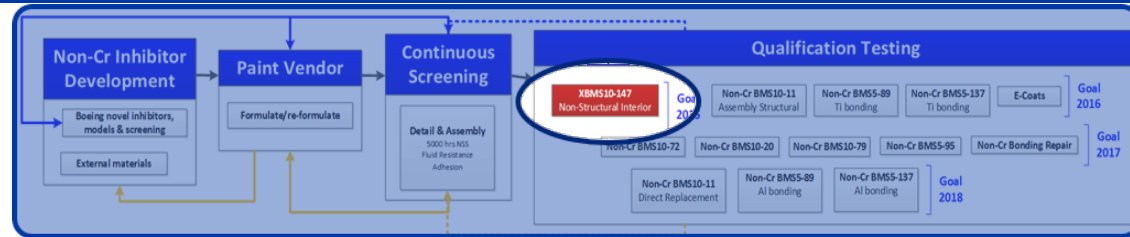
- Corrosion resistance criteria based on MIL-PRF-23377, but with a wider scribe.
  - Neutral Salt Spray (NSS) for 2000 hrs, no pitting & minimal oxides within the scribe.
- Compatibility requirement testing based on application

### Opportunities

- Interior payloads primer for non-structural parts (brackets, clips, stow-bin rails, etc...) – All models
- Systems Line Replaceable Units (LRU), such as ducts, valves, pumps, etc...) – 777X

### Status:

- 7 candidates tested, top candidate reformulated for improved adhesion (blisters)
  - Reformulation successful, candidate currently in qual testing

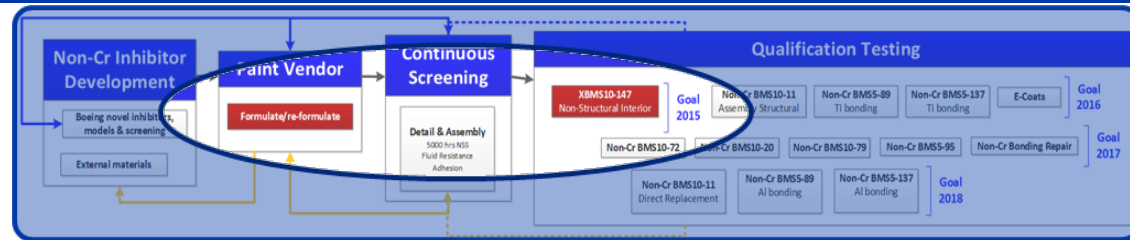


Key Tests	Application: Payloads, Systems, Both	8	7	6	5	4	3	2	1
Spray Properties	Both	TBD	PASS	PASS	MARGINAL	PASS	PASS	FAIL	PASS
Drying Properties	Both	PASS SCREENING	PASS	FAIL	PASS	PASS	PASS	PASS	PASS
Color	Payloads	PASS SCREENING	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Gloss	Payloads	TBD	PASS	FAIL	FAIL	PASS	FAIL	FAIL	PASS
Adhesion	Both	PASS SCREENING	FAIL BLISTERS	PASS	PASS	FAIL	FAIL	MARGINAL	FAIL
Humidity	Both	PASS SCREENING	FAIL BLISTERS	PASS	PASS	FAIL	FAIL	PASS	FAIL
Neutral Salt Fog 2000 hrs	Both	TBD	PASS EXCELLENT	PASS ACCEPTABLE	FAIL	PASS GOOD	FAIL	FAIL	FAIL
Fluid Resistance	Both	PASS SCREENING	PASS	FAIL	PASS	PASS	FAIL	PASS	PASS
Rivets & Fasteners Adhesion	Both	PASS SCREENING	FAIL BLISTERS	PASS	--	FAIL	--	FAIL	FAIL

### Compatibility requirements by application:

Materials	Payloads Applications	Both	Systems Applications
Substrates		2000 series bare	Al Castings
		7000 series bare	Ti 6Al-4V
		6000 series bare	CRES
Substrate Prep	BSAA Unsealed	BSAA Sealed	Grit Blast
	CAA Unsealed	Alodine 600	Cd plating, Cr6+
	Sol-Gel	Alodine 1200	Zn-Ni plating, Cr3+
Fluids		BMS3-11	TCP (Navy Cr3+)
		Fuel	BMS3-32 Ty II
		Water	
Primers	BMS10-11 Ty I Gr A	PR-1200 RTV	
	BMS10-11 Ty I Gr B		
	BMS10-11 Ty I Gr E		
Topcoats	BMS10-83 Ty IV	BMS10-60 Ty I	BAC5710 Ty 41
	BMS10-83 Ty II		
Sealants	BMS10-83 Ty VII	BMS10-11 Ty II	
	BMS5-142		
Adhesives		BMS5-45	
		BAC5010 Ty 60	
		BAC5010 Ty 70	
		BAC5010 Ty 89	

# XBMS10-147 Top Candidate



## Curing Solution Reformulation

- 5 candidates screened
- Tested Fresh vs Aged 4 months @ 120F
- Chemistry vs mechanical properties

## Liquid Component Testing

- HPLC
- FTIR
- GPC
- LCMS

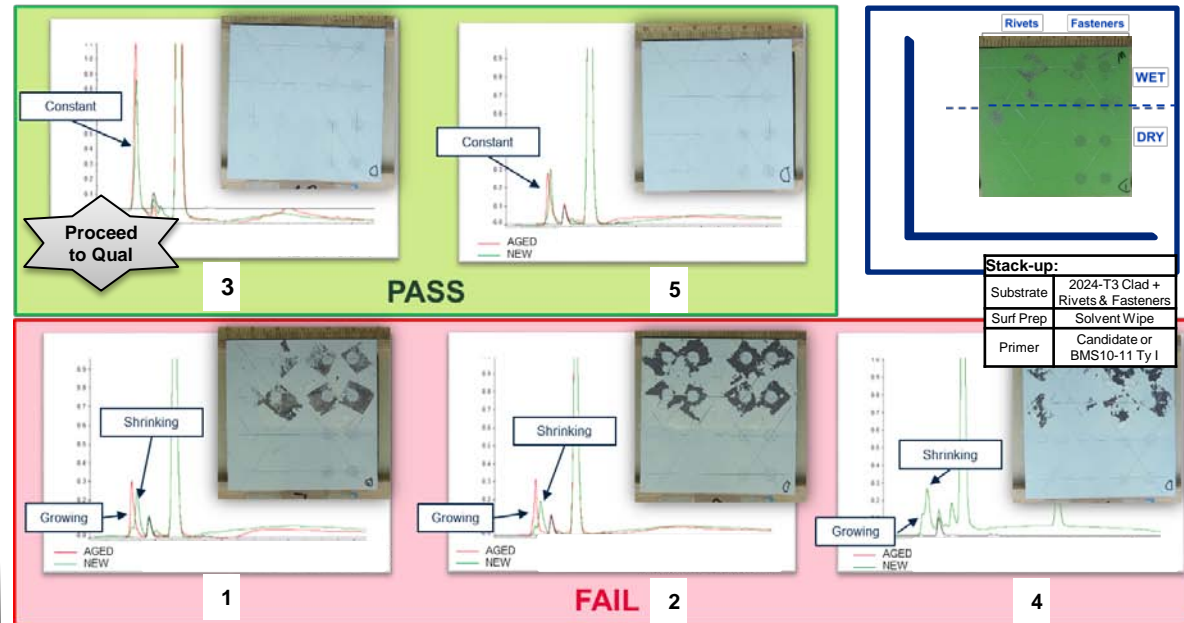
## Cured Film Testing

- Rivets/Fasteners Adhesion
- Wet/Dry Adhesion
- 120F Condensing Humidity
- SEM/EDS

## Top re-formulation proceeding to qual

- 1<sup>st</sup> production Batch sprayed Sept 2014

## Curing solution chemistry aging vs cured film adhesion properties

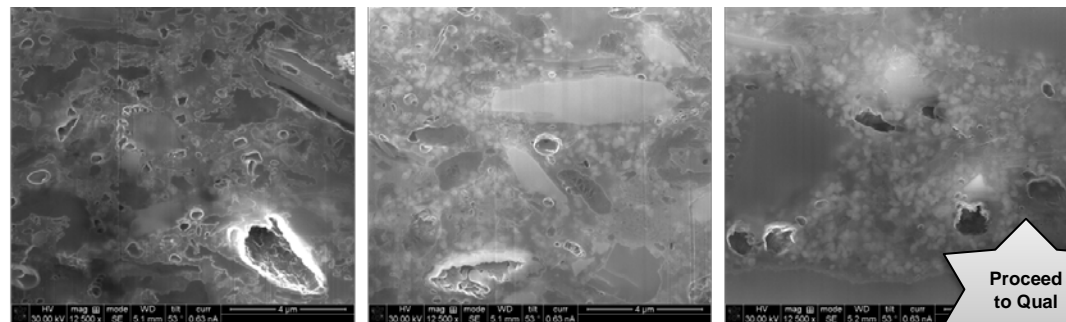


## Curing solution components per reformulation.

candidate	initial	1	2	3	4	5
part	B	B	B	B   C	B   C	B   C
Components						
Adh. Rivets & Fasteners	FAIL	FAIL	FAIL	PASS	FAIL	PASS

Proceed to Qual

## SEM – focused ion beam paint cross-section at 12,500x mag



initial

4

3

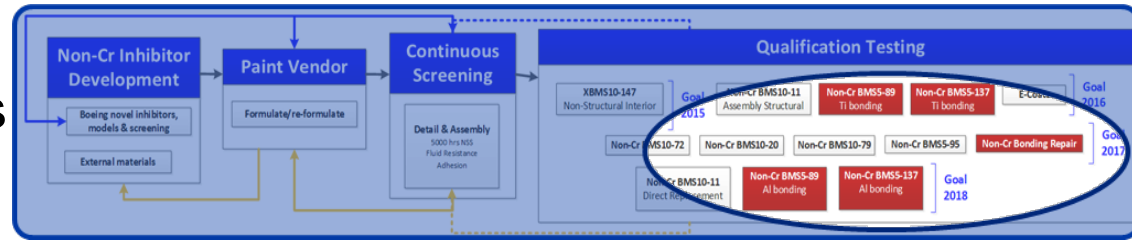
Proceed to Qual

Part 11



# Adhesive Bond Primer

## High/Medium/Low risk zones



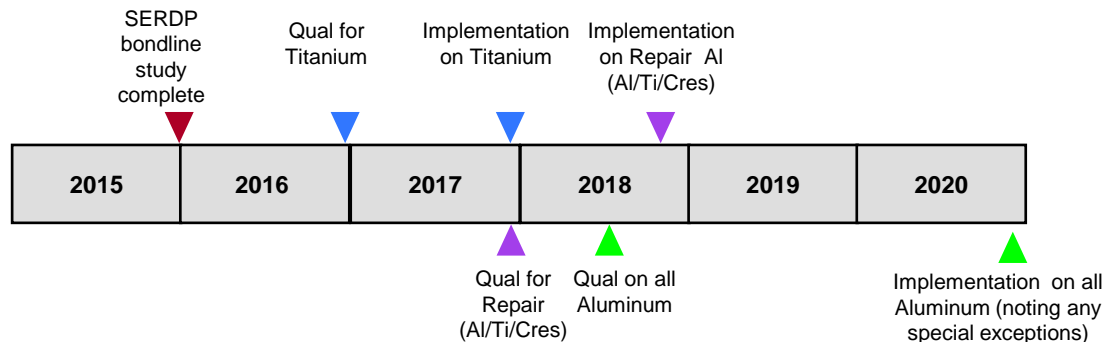
## Overview

- Two candidates selected based on performance over on titanium/sol-gel and aluminum/PAA substrates
- The desired goal is to find a primer that can do both aluminum and titanium bonding at both 250F and 350F processing temperatures

## Key Tests

- Wide Area Lap Shear - *BSS7202 Type III*
- Metal to Metal Peel - *BSS7206 Class 1, ASTM D 1781*
- Salt Spray – *Scribed panels, ASTM B117*
- Wedge Crack – *BSS7448 ASTM D 3762*

## Qual & Implementation Goals:



## Bond Primers are Applied on Variety of Surface Treatments and Alloys

Aluminum	Non-Aluminum: Titanium, Stainless Steel, Nickel
aluminum adherend 2024-T3 bare	titanium adherend Ti-6Al-4V
phosphoric acid anodize	1 - Grit Blast 2 - Grit Blast + NaOH 3 - Etch + NaOH
Bond Primer (0.15-0.40 ml / 6400 nm)	Bond Primer (0.15-0.40 ml / 6400 nm)
Adhesive (film) 10 ml	Adhesive (film) 10 ml
Bond Primer (0.15-0.40 ml / 6400 nm)	Bond Primer (0.15-0.40 ml / 6400 nm)
phosphoric acid anodize	1 - Grit Blast 2 - Grit Blast + NaOH 3 - Etch + NaOH
aluminum adherend 2024-T3 bare	titanium adherend Ti-6Al-4V

*thin bond primer layer* (0.002-0.004mil / 50-100nm)



## Boeing Specifications:

- BMS 5-89
- MMS350, Ty III
- MMS307, Type II
- HMS 16-1111, Ty 1
- HMS 16-1278, Ty 1
- BMS 5-137
- DMS 2002, Ty 3 & 4
- DMS 2169, Ty 1(A)
- SCGMS56033, Class 2

The diagram illustrates the process flow for the development of a new paint formulation. It begins with **Non-Cr Inhibitor Development**, which involves boiling novel inhibitors, models & screening, and using external materials. This leads to the **Paint Vendor**, who formulates or re-formulates the paint. The process then moves to **Continuous Screening**, which includes detail & assembly testing for 5000 hrs NSS, fluid resistance, and adhesion. This is followed by **Qualification Testing** for various applications, categorized by goal years: Goal 2015 (XBMS10-147 Non-Structural Interior, Non-Cr BMS10-11 Assembly Structural, Non-Cr BMS-89 Ti bonding, Non-Cr BMS-137 Ti bonding, E-Costs), Goal 2017 (Non-Cr BMS10-72, Non-Cr BMS10-20, Non-Cr BMS10-79, Non-Cr BMS-95, Non-Cr Bonding Repair), and Goal 2018 (Non-Cr BMS10-11 Direct Replacement, Non-Cr BMS-89 Al bonding, Non-Cr BMS-137 Al bonding). A red circle highlights 'E-Costs' in the Goal 2015 section.

- Automated, low waste process which provides uniform paint film thickness.

- Potential use for complex geometries, such as tubes in low corrosion-risk zones
- One candidate has passed screening tests, with varying degrees of corrosion protection depending on metal alloy.

Electrophoretic Deposition	Electrostatic Spray
 <p>smooth and uniform thickness on corners and interior</p>	 <p>corners and recessed areas have less coverage</p>



# Gaps & Long Term Developments

## Gaps:

- In-service testing and long term exposure. Will not be accepted until proven in service.
  - 50-100k cycles per commercial aircraft
  - Lifecycle of 20+ years
  - Corrosion observed after 8-10 years in-service for Cr
- Risks associated with unknown failure of primary structure
  - Flight and safety critical components
    - Interaction between corrosion effects and fatigue crack initiation is unknown
- Reliable inspection methods
  - Implement nonchromate systems with increased inspection
  - Understand relationship between corrosion morphology and fatigue initiation/propagation
- Risk based implementation increases manufacturing complexity
  - Ensuring the correct coating system on the correct application

## Current Authorization Needs: List 3 and 4 Chromates

Identification			Authorisation Dates		REACH Authorization Needed		
List	Substance	CAS	Last Application	Sunset	BCA	BDS	Combined
3	Ammonium Dichromate	7789-09-5	3/21/2016	9/21/2017	NO	NO	NO
3	Chrome Trioxide	1333-82-0			YES	YES	YES
3	Chromic Acid, hydrated forms	7738-94-5 & 13530-68-2			YES	YES	YES
3	Potassium Chromate	7789-00-6			NO	NO	NO
3	Potassium Dichromate	7778-50-9			YES	YES	YES
3	Sodium Chromate	7775-11-3			YES	YES	YES
3	Sodium Dichromate	7789-12-0 & 10588-01-9	7/22/2017	1/22/2019	YES	YES	YES
4	Dichromium tris (chromate)	24613-89-6			NO	NO	NO
4	Pentazinc Chromate Octahydroxide	49663-84-5			NO	NO	NO
4	Potassium hydroxyoctaoxidizincate dichromate	11103-86-9			YES	YES	YES
4	Strontium Chromate	7789-06-2			YES	YES	YES

**BCA Chemical Risk Management is interested in discussing partnering opportunities in the chromate use application process**

